XVI International Mineral Processing and Recycling Conference
28-30 May 2025, Belgrade, Serbia

DOI: 10.5937/IMPRC25226Z Original research article

UV-VIS IDENTIFICATION OF COPPER COMPLEXES WITH INHIBITOR ORGANIC COMPONENTS IN THE ELECTROLYTE

Milica Zdravković[1,#], 0000-0001-9488-9151,
Vesna Grekulović[1], 0000-0001-6871-4016,
Edina Huseinović[2], 0009-0007-0222-383X,
Robert Vianello[3], 0000-0003-1779-4524,
Nada Štrbac[1], 0000-0003-4836-1350,
Melita Huremović[2], 0009-0001-5143-0356,
Milan Gorgievski[1], 0000-0002-9899-719X,
[1]University of Belgrade, Technical Faculty in Bor, Bor, Serbia
[2]University of Tuzla, Faculty of Natural Sciences and Mathematics, Tuzla, Bosnia and Herzegovina
[3]Laboratory for the Comp. Design and Synthesis of Functional Materials, Ruđer Bošković Institute, Zagreb, Croatia

ABSTRACT – The UV-VIS method is an effective, non-destructive method that enables a better understanding of the electrolyte during corrosion. The aim of the study presented in this paper is to determine the existence of an organometallic complex in a 0.5 M NaCl solution with the addition of *Rubus fruticosus L.* leaf extract (RFLE). The experiments were conducted in a 0.5 M NaCl solution with the addition of RFLE (5 g/L and 10 g/L) with and without the immersion of a copper coupon. The results show that after the copper coupon standing in the electrolyte, there is a change in the absorbance maximum in the solution with 5 g/L RFLE, while no change is observed in the solution with 10 g/L RFLE. Such a change indicates the existence of a copper-RFLE complex in the solution with lower inhibitor concentration. In the case of RFLE, forming a copper complex with caffeic acid, isoquercetin and astragalin is possible. The absence of the complex at a concentration of 10 g/L RFLE can be attributed to a change in the mechanism and the lack of copper ions in the solution due to adequate corrosion protection.

Keywords: UV-VIS, Organometallic Complex, Corrosion Inhibitor, *Rubus fruticosus L.*

INTRODUCTION

Corrosion of copper in saline environments, especially in 3.5% sodium chloride (NaCl) solutions, is challenging because it causes destruction of the metal that has major industrial applications, leading to significant economic losses and safety concerns [1]. One of the ways to reduce the metal corrosion rate is the application of corrosion inhibitors [2]. However, corrosion inhibitors, often synthetic and toxic, raise environmental issues that require the exploration of viable alternatives [3]. Plant

[#] corresponding author: mzdravkovic@tf.bor.ac.rs

extracts are effective alternatives to conventional corrosion inhibitors [4].

Blackberry leaf extract (*Rubus fruticosus L.* leaf extract, RFLE) is a very effective copper corrosion inhibitor in 0.5 M NaCl. The maximum corrosion inhibition efficiency (99.1%) was determined, after standing for 10 days, at room temperature, in a solution of 0.5 M NaCl with the addition of 15 g/L RFLE [5]. Recent research notes important parameters to consider when discussing the application of environmental inhibitors. Solvents used to obtain the extract, sustainability, availability of the plant, toxicity of the extraction process, and costs of collecting and cleaning the plant were taken as important factors [6]. Since RFLE is obtained by extraction from water, a process similar to obtaining tea, it is a by-product of the production of blackberry fruit that is in excess compared to the needs of tea production, while preventing its burning on the plantation, this extract does not indicate the disadvantages mentioned earlier [7]. In addition to the investigation of RFLE as a copper corrosion inhibitor in a chloride environment at concentrations from 2 g/L to 15 g/L, it was determined that a complex is formed in the solution with the addition of 15 g/L RFLE. The physical adsorption occurs on the copper surface, which takes place according to the Langmuir adsorption isotherm. However, since it was determined by applying the electrochemical impedance method that two different adsorption mechanisms occur, it is necessary to additionally examine whether the formation of complexes occurs in the presence of 5 g/L and 10 g/L RFLE. Namely, the corrosion process is primarily controlled by diffusion (at concentrations lower than 15 g/L RFLE), after which it is controlled by charge transfer (at 15 g/L RFLE) [5, 8].

The UV-VIS method is an effective method for identifying metal complexes with corrosion inhibitor organic compounds [9, 10]. UV–Vis spectroscopy is a cost-effective, simple, versatile, non-destructive, and analytical technique. It is suitable for a large spectrum of organic compounds and some inorganic species. As a function of wavelength, UV–Vis spectrophotometers measure the absorption or transmission of light that passes through a medium [11]. The change in electrolyte absorbance in the presence of metal enables the identification of the organometallic complex, which allows the understanding of the corrosion inhibition process complexity due to the large number of species participating in the corrosion reactions [8-10].

EXPERIMENTAL

Materials and Sample Preparation

The oxygen-free phosphor copper sheet Cu-DHP (99.9% Cu, 0.0198% P, 0.0005% Pb) was used for making copper coupons. The copper sheet was cut to dimensions of 1 × 1 cm using an erozimate machine with a precision of 0.001 mm, to achieve the most precise cutting and reduce the copper crystal lattice damage. A 0.5 M NaCl solution was prepared using distilled water and the appropriate amount of NaCl salt p. a. purity manufactured by “Zorka Pharma”, Serbia. The RFLE was added to obtain 0.5 M NaCl with the addition of 5 and 10 g/L. Aqueous blackberry leaf extract was prepared from dried blackberry leaves manufactured by “Adonis”, Sokobanja, Serbia and distilled water. The solid: liquid ratio was 2 (kg): 15 (L). The leaves were poured with hot distilled water (95°C). The mixture was filtered after 12 h with cotton cloth and filter paper No1. Aqueous blackberry leaf extract was then evaporated on a rotary evaporator Buchi R-210

(BUCHI Labortechnik AG, Switzerland) at 72 mbar at 40°C. Evaporation was completed after obtaining a resin-like solvent-free extract. Working solutions were prepared before experiments. All experiments were performed at room temperature.

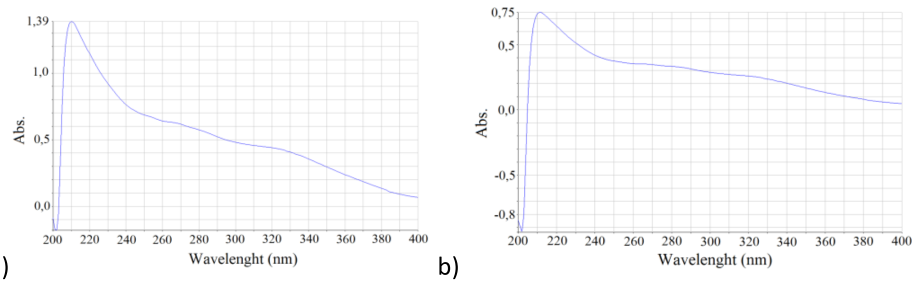
UV–VIS Spectroscopy

The UV–VIS method was used to interpret the possibility of the RFLE-copper complex formation in 0.5 mol/L NaCl. The experiments were performed in 0.5 M NaCl solution with the addition of 5 g/L and 10 g/L RFLE before and after the immersion of copper coupons for 24 h. The experiments were performed in the wavelength range of 200–400 nm using a UV–Vis spectrometer Lambda 25 (Perkin Elmer, USA).

RESULTS AND DISCUSSION

The UV-VIS results for the 0.5 M NaCl solution with the addition of 5 g/L RFLE before and after the immersion of the copper coupon are shown in figures 1a and 1b. Both UV-VIS spectra show absorption maxima at around 210 nm. No significant change in the absorption spectrum shape is observed when copper is added to the solution. However, a change in the absorbance maximum is observed, with a significant decrease in the maximum in the presence of copper. According to the literature, this change indicates the formation of a RFLE-copper complex [9, 10]. The corresponding absorption can be attributed to π–π* and n–π* electron transitions [9, 10, 12].

The π-π* transition is otherwise called the K band. It occurs in compounds with unsaturated centers (simple alkenes, aromatic compounds, carbonyl compounds). This transition requires less energy than the n-σ* transition. The n-π* transition is otherwise called the R band. In this case, the electron that does not belong to the shared electron pair of the hetero atom is excited into the π* antibonding orbital. In the case of aliphatic ketones, this transition occurs at about 280 nm and is the transition with the lowest energy [13].



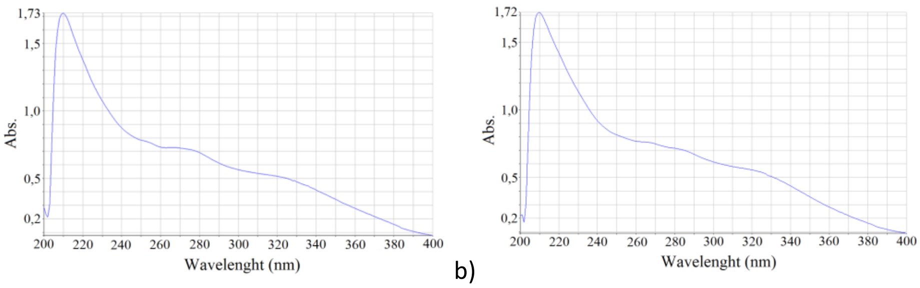
a) b)

Figure 1 UV–Vis spectra of the 0.5 M NaCl with 5 g/L RFLE (a) before and (b) after 24 h of copper coupon immersion

In an earlier investigation, the HPLC method determined the presence of three compounds in RFLE: caffeic acid, quercetin-3-O-glucoside and kaempferol-3-glucoside [8]. Each of these compounds can potentially form a complex with the copper ions present in the electrolyte. The results of research on metal chelation with flavonoids for the characterization of antioxidants indicate that flavonoids can form high-affinity complexes with transition metals, most often copper and iron [14, 15]. Copper (II) chloride is often used as a starting substance for the formation of organometallic complexes [14]. Based on the E-pH diagram and the pH value of the tested solutions of about 5.6, it is clear that during the corrosion process, the transfer of copper(II) ions into the solution occurs [16]. In this way, copper ions can form an organometallic complex with RFLE molecules.

Many studies point to the possibility of the copper complexes formation with all three organic compounds present in RFLE. Research confirms the formation of a caffeic acid complex with Cu(II) in NaCl solution [17]. Earlier studies showed that a complex is formed between copper ions and quercetin glucosides [18]. The stoichiometry of metals and flavonoids is 2:1 in the case of the complex formation with Fe (II), Ni (II), Co (II), and Zn (II), while with Cu (II) the mechanism is different. This happens due to simultaneous oxidation, because Cu (II) has a stronger oxidative activity and quercetin is more easily oxidized under acidic conditions [18, 19]. Organometallic complexes of kaempferol with Cu(II) ion were investigated in terms of antioxidant and prooxidative behavior. The results of this research indicate the formation of two types of complexes (1:1 and 1:2) [20].

UV-VIS results for the 0.5 M NaCl solution with the addition of 10 g/L RFLE before and after the immersion of the copper coupon are shown in figures 2a and 2b.



a) b)

Figure 2 UV–Vis spectra of the 0.5 M NaCl with 10 g/L RFLE (a) before and (b) after 24 h of copper coupon immersion

In contrast to the previous change in absorbance, at a concentration of 10 g/L RFLE, no change in the UV-VIS spectrum occurs when the copper coupon is added. These results indicate that at a sufficiently high concentration of the inhibitor, there is a significant reduction in metal corrosion, so there are no copper ions present in the solution that would enable the formation of an organometallic complex. At higher concentrations than 10 g/L RFLE, the appearance of unstable complexes is expected, due to a change in the mechanism [5].

CONCLUSION

Using the UV-VIS method, UV-VIS spectra were obtained in 0.5 M NaCl solution with addition of 5 g/L and 10 g/L RFLE before and after immersion of the copper coupon. it was determined that in a solution with a lower concentration of corrosion inhibitor (5 g/L RFLE), the formation of organometallic complexes occurs. It is possible to create different complexes considering the complexity of the electrolyte composition. A caffeic acid, quercetin-3-O-glucoside and kaempferol-3-glucoside complexes with Cu(II) ions can be formed. The absence of an absorbance change at higher concentration can be attributed to the lack of copper ions in the solution, due to the adequate anti-corrosion effect of RFLE.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration no. 451-03-137/2025-03/200131. The experiments were carried out within the ERASMUS KA107 mobility (1.4.-5.7.2022.) at the Faculty of Technology, University of Tuzla (Bosnia and Herzegovina).

REFERENCES

1. Gapsari, F., Hadisaputra, S., Sulaiman, A.M., Ebenso, E., Thakur, A., Kumar, A. (2024) Eco-friendly corrosion inhibition of copper in NaCl media using *Perseana americana* extract: Insights from quantum and electrochemical studies. Results in Surfaces and Interfaces, 17, 100327.
2. Dariva, C.G., Galio, A.F. (2014) Corrosion inhibitors–principles, mechanisms and applications. Developments in corrosion protection, 16, 365-378.
3. Njoku, C.N., Maduoma, T.U., Emori, W., Odey, R.E., Unimke, B.M., Yakubu, E., Anorondu, C.C., Udunwa, D.I., Njoku, O.C., Oyoh, K.B. (2024), Natural and synthetic drugs as eco-friendly and sustainable corrosion inhibitors for metals: a review. Pigment & Resin Technology, 53 (6), 1074-1087.
4. Dehghani, A., Ghahremani, P., Mostafatabar, A.H., Ramezanzadeh B. (2024) Plant extracts: Probable alternatives for traditional inhibitors for controlling alloys corrosion against acidic media—A review. Biomass Conversion and Biorefinery, 14, 7467–7486
5. Zdravković, M., Grekulović, V., Suljagić, J., Štrbac, N., Marković, I., Gorgievski, M., Marković, M. (2024) The *Rubus fruticosus* Leaf Extract as an Eco-Friendly Copper Corrosion Inhibitor. Protection of Metals and Physical Chemistry of Surfaces, 1-0.
6. Verma, C., Alfantazi, A., Quraishi, M.A., Rhee, K.Y. (2023) Are extracts really green substitutes for traditional toxic corrosion inhibitors? Challenges beyond origin and availability. Sustainable Chemistry and Pharmacy, 31, 100943.
7. Zdravković, M., Grekulović, V., Štrbac, N., Zdravković, B., Gorgievski, M., Marković, M., Marković, M. (2024) Raspberries and blackberries grown in Serbia from the perspective of the Green Agenda. ECOLOGICA, 31 (114), 137-143.
8. Zdravković, M., Grekulović, V., Suljagić, J., Stanković, D., Savić, S., Radovanović, M., Stamenković, U. (2023) Influence of blackberry leaf extract on the copper corrosion behaviour in 0.5 M NaCl. Bioelectrochemistry, 151.
9. Grudić, V., Bošković, I., Gezović, A. (2018) Inhibition of Copper Corrosion in NaCl Solution by Propolis Extract. Chemical and Biochemical Engineering Quarterly, 32 (3), 299.

10. Gadow, H.S., Motawea, M.M., Elabbasy, H.M. (2017) Investigation of myrrh extract as a new corrosion inhibitor for α-brass in 3.5% NaCl solution polluted by 16 ppm sulfide, RSC Advances, 47.
11. Khalid, K., Ishak, R., Chowdhury, Z. Z. (2024) Chapter 15 - UV–Vis spectroscopy in non-destructive testing. Non-Destructive Material Characterization Methods (A. Otsuki, S. Jose, M. Mohan, S. Thomas), Elsevier, 391-416.
12. Sherif, E.M., Park, Su-M. (2005) Inhibition of Copper Corrosion in 3.0% NaCl Solution by N-Phenyl-1,4-phenylenediamine. Journal of The Electrochemical Society, 152 (10), B428.
13. Kalsi, P. S. (2004) Spectroscopy of Organic Compounds. 6th edition, New age international publishers, New Delhi.
14. Mira, L., Tereza Fernandez, M., Santos, M., Roch, R., Helena, Florênci, M., Jennings, K.R. (2002) Interactions of Flavonoids with Iron and Copper Ions: A Mechanism for their Antioxidant Activity. Free Radical Research, 36 (11), 1199–1208.
15. Kejik, Z., Kaplanek, R., Masarik, M., Babula, P., Matkowski, A., Filipensky, P., Vesela, K., Gburek, J., Sykora, D., Martasek, P., Jakubek M. (2021) Iron Complexes of Flavonoids-Antioxidant Capacity and Beyond. International Journal of Molecular Sciences, 22 (2), 646.
16. Alfantazi, A.M., Ahmed, T.M., Tromans, D. (2009) Corrosion behavior of copper alloys in chloride media. Materials & Design, 30 (7), 2425-2430.
17. De Stefano, C., Foti, C., Giuffrè, O., Sammartano, S. Acid–base and UV behavior of 3-(3,4-dihydroxyphenyl)-propenoic acid (caffeic acid) and complexing ability towards different divalent metal cations in aqueous solution. Journal of Molecular Liquids, 195, 9-16.
18. Liu Y, Guo M. (2015) Studies on transition metal-quercetincomplexes using electrospray ionization tandem mass spec-trometry. Molecules 20, 8583-8594.
19. Lee, J., Kim, O.-H., Jung, B.-K., Cho, I.-S., Lee, Y.-J., Choi, H.-J., Kim, Y.-C., Oh, Y.-H., Jung, K., Cha, S.-H., Jang, K.-Il. (2019) Influence of Mineral Supplementation on the Results from Analysis of Flavonol Glycoside Content in Ginkgo biloba Dietary Supplements. Preventive nutrition and food science. 24.
20. Simunkova, M., Barbierikova, Z., Jomova, K., Hudecova, L., Lauro, P., Alwasel, S.H., Alhazza, I., Rhodes, C.J., Valko, M. (2021) Antioxidant vs. Prooxidant Properties of the Flavonoid, Kaempferol, in the Presence of Cu(II) Ions: A ROS-Scavenging Activity, Fenton Reaction and DNA Damage Study. International Journal of Molecular Sciences, 22 (4), 1619.